Synthesis and Self-Assembly of Well-Defined Cyclodextrin-Centered Amphiphilic $A_{14}B_7$ Multimiktoarm Star Copolymers Based on Poly(ε-caprolactone) and Poly(acrylic acid)

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ABSTRACT: Novel amphiphilic $A_{14}B_7$ multimiktoarm star copolymers composed of 14 poly(ε-caprolactone) (PCL) arms and 7 poly(acrylic acid) (PAA) arms with β-cyclodextrin (β-CD) as core moiety were synthesized by the combination of controlled ring-opening polymerization (CROP) and atom transfer radical polymerization (ATRP). 14-Arm star PCL homopolymers (CDSi-SPCL) were first synthesized by the CROP of CL using per-6-(*tert*-butyldimethylsilyl)-β-CD as the multifunctional initiator in the presence of $Sn(Oct)_2$ at 125 °C. Subsequently, the hydroxyl end groups of CDSi-SPCL were blocked by acetyl chloride. After desilylation of the *tert*-butyldimethylsilyl ether groups from the β-CD core, 7 ATRP initiating sites were introduced by treating with 2-bromoisobutyryl bromide, which further initiated ATRP of *tert*-butyl acrylate (*t*BA) to prepare well-defined $A_{14}B_7$ multimiktoarm star copolymers [CDS(PCL-P*t*BA)]. Their molecular structures and physical properties were in detail characterized by ^{1}H NMR, SEC-MALLS, and DSC. The selective hydrolysis of *tert*-butyl ester groups of the P*t*BA block gave the amphiphilic $A_{14}B_7$ multimiktoarm star copolymers [CDS(PCL-PAA)]. These amphiphilic copolymers could self-assemble into multimorphological aggregates in aqueous solution, which were characterized by dynamic light scattering (DLS), transmission electron microscopy (TEM) and atomic force microscopy (AFM). © 2010 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 48: 2961–2974, 2010

KEYWORDS: amphiphiles; atom transfer radical polymerization (ATRP); controlled ring-opening polymerization (CROP); micelles; miktoarm star copolymer; poly(ε-caprolactone); poly (acrylic acid); poly(*tert*-butyl acrylate); ring-opening polymerization; self-assembly; self-organization; star polymers

INTRODUCTION Miktoarm star copolymers consisting of arms with different chemical nature emanating from one central core have evoked considerable attention because of their unique morphological and physical properties in the solid state as well as in solution.[1,2] Originally, miktoarm star copolymers were synthesized from diphenylethylene derivatives or chlorosilane via living anionic polymerization.[3–8] However, these methods are restricted to few monomer and involving strict polymerization conditions. Until recently, controlled/living polymerization methods (CLP), such as controlled ring-opening polymerization (CROP),[9] atom transfer radical polymerization (ATRP),[10–12] nitroxide mediated radical polymerization (NMP),[13] and radical addition fragmentation polymerization (RAFT)[14] have proved to be efficient methods to design well-defined and complex macromolecular architectures because of the broad variety of applicable monomers and benign polymerization conditions. Moreover, the appearance of "click reactions"[15] also provides a powerful method for the synthesis and functionalization of polymers with unique structures.[16–18] Therefore, by the combination of CLP techniques or "click reactions," various types of miktoarm star copolymers with varying chemical composition and molecular topology have been synthesized.[19–34] Typically, Gnanou and coworkers demonstrated that AB_2 miktoarm star polymers can be prepared by ATRP and chemical modification of ATRP-derived ω-halogeno precursors.[35] Hadjichristidis and Dumas prepared A_2B_2 miktoarm star polymers by the combination of CROP of ε-caprolactone (CL) and ATRP of styrene (St) or *tert*-butyl methacrylate (*t*BMA) based on a heterotetra functional initiator.[36–38] Hedrick and coworkers prepared A_3B_3 miktoarm star copolymers containing poly(ε-caprolactone) (PCL) and poly(methyl methacrylate) (PMMA) arms using tandem CROP and ATRP with a miktofunctional initiator.[39] Zhao's group reported ABC miktoarm star copolymers by a three-step synthesis consisting of CROP of CL, ATRP of MMA and NMP of St from a trifunctional initiator.[40] Very recently, Wang and coworkers also described the synthesis of amphiphilic ABC miktoarm star copolymers by the combination of CROP and "click reactions."[41]

Additional Supporting Information may be found in the online version of this article. Correspondence to: W.-P. Zhu (E-mail: carrols@163.com) or Z.-Q. Shen (E-mail: zhiquan_shen@163.com)

Furthermore, to obtain new miktoarm star copolymer models for the investigation of architecture-property relationships and seek for new applications in biomedical materials, nanotechnology and supermolecular science, the design and synthesis of miktoarm star copolymers with novel and complex architectures is of great importance. A_nB_m multimiktoarm star copolymer with more than 10 arms is one of the most complicated miktoarm star copolymers which are rarely synthesized by simply utilizing CLP techniques. Recently, Matyjaszewski and coworkers introduced a new method to synthesize A_nB_m multimiktoarm star copolymers by one-pot ATRP crosslinking reaction of several different linear macroinitiators and a divinyl crosslinker. The average arm numbers of these synthesized miktoarm star copolymers can be extended to 50.[42–45] Likewise, Wiltshire and Qiao also prepared A_nB_m multimiktoarm star copolymers by crosslinking of ω-halogeno PCL and PMMA using ethylene glycol dimethacrylate (EGDMA) as crosslinker.[46] However, in these cases, neither the exact arm numbers nor the precise architecture of the miktoarm star copolymers could be controlled. An alternate method to construct well-defined A_nB_m multimiktoarm star copolymers with precise arm numbers and lengths would resort to designing a heteromultifunctional A_nB_m initiator which is able to initiate different polymerizations independently and sequentially. Nevertheless, it is inconceivable to synthesize an A_nB_m initiator with more than 10 functionalities from small molecules. Fortunately, naturally occurring cyclodextrins (including α-CD, β-CD, and γ-CD), which have fixed numbers of primary and secondary hydroxyl groups with different activities, provide excellent platforms to design A_nB_m heteromultifunctional initiators for the synthesis of well-defined multimiktoarm star copolymers. During the past few years, several research groups have focused on the synthesis of CD-centered star polymers.[47–52] For example, Kakuchi and coworkers reported the umbrella-like multimiktoarm star copolymers (AB_{20}) synthesized from a β-CD derivative by the combination of NMP and ATRP.[53] However, the controllability of the polymerization is lost to some extent in the ATRP step, well-defined AB_{20} miktoarm star copolymers must be fractionated by preparative size exclusion chromatography.

Considering the biocompatibility and biodegradability of cyclodextrins, fabricating CD-based biocompatible multimiktoarm star copolymers in relation to potential biomimetic materials seems to be very attractive. Controlled ring-opening polymerization (CROP) of cyclic lactones, lactides and carbonates is one of the most convenient methods to synthesize biocompatible polymers. Thereby, in this article, well-defined biocompatible amphiphilic $A_{14}B_7$ multimiktoarm star copolymers based on β-CD have been synthesized by utilizing CROP of ε-caprolactone (CL), ATRP of *tert*-butyl acrylate (*t*BA) and selective hydrolysis from a β-CD derivative [per-6-(*tert*-butyldimethylsilyl)-β-CD] (Scheme 1).

Meanwhile, it is well-known that the architecture of amphiphilic copolymer is one of the primary factors that influences the morphology and dimension of the polymeric self-assembly aggregates.[54,55] Up to date, various amphiphilic copolymers with complex structures such as graft,[56] star block,[57] and dendrimer[58] have been synthesized and used for self-assembly. However, the study on the self-assembly originating from miktoarm star copolymers is still quite limited.[59–61] Some unique self-assembly behaviors of ABC miktoarm star copolymer have been reported by Lodge and coworkers.[62–64] It is expected that complex multimiktoarm star copolymers will self-assemble into novel aggregates in selective solvent. Thus, in this article, the self-assembly behaviors of amphiphilic $A_{14}B_7$ multimiktoarm star copolymers in aqueous solution were investigated by dynamic light scattering (DLS), transmission electron microscopy (TEM), and atomic force microscopy (AFM).

EXPERIMENTAL

Materials

β-Cyclodextrin hydrate (β-CD) was dried over P_2O_5 at 80 °C under reduced pressure overnight before use. Pyridine, toluene, triethylamine (TEA) were dried over CaH_2 and distilled just before use. THF was distilled from the ketyl prepared from sodium and benzophenone. ε-Caprolactone (ε-CL, 99%; Acros) and *tert*-butyl acrylate (*t*BA; 99%; Aldrich) were distilled under reduced pressure before use. Acetic chloride (AcCl; 99%; Aldrich) was distilled just before use. *N,N,N′,N″,N″*-Pentamethyldiethylenetriamine (PMDETA; 99%; Aldrich), 2-bromisobutyryl bromide (97%; Aldrich), and *tert*-butylchlorodimethylsilane (TBDMSCl; 98%; Acros) were used as received. CuBr (99%; Acros) was purified by stirring overnight in acetic acid, after filtration, it was washed with ethanol and then dried in vacuum. Boron trifluoride diethyl etherate ($BF_3{\cdot}Et_2O$; 48% BF_3), stannous octoate [$Sn(Oct)_2$; 97%] and other reagents were purchased from Sinopharm Chemical Reagent, (China) and used as received.

Measurements

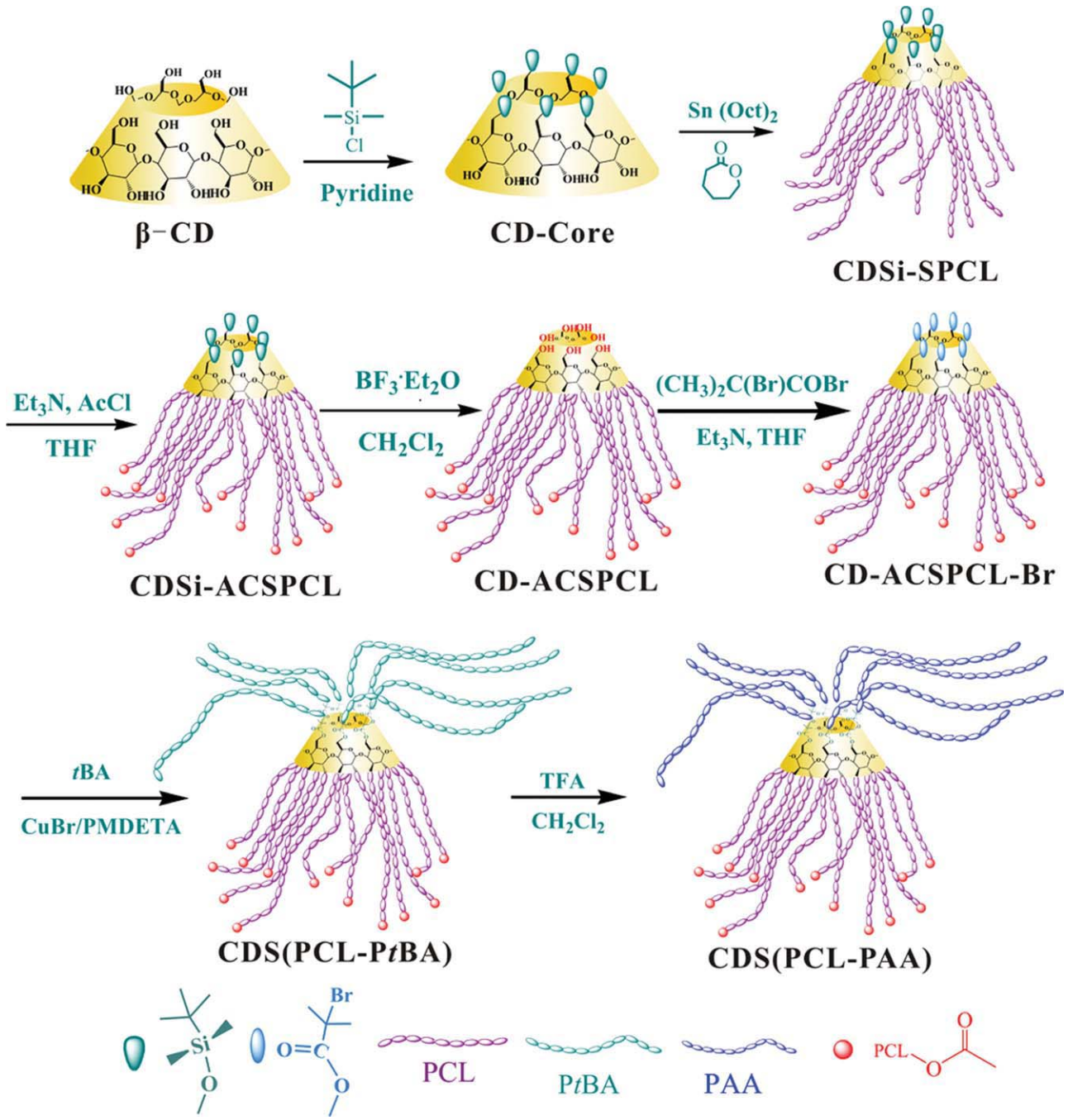
^{1}H NMR spectra were recorded on a Bruker Avance DMX500 spectrometer in $CDCl_3$ with tetramethylsilane as internal standard.

ESI-positive MS was performed using Bruker Esquire 3000 plus spectrometer with an ESI interface.

The molecular weight and molecular weight distribution were determined by size-exclusion chromatography/multiangle laser light scattering (SEC-MALLS). The size-exclusion chromatography (SEC) system consisted of a Waters degasser, a Waters 515 HPLC pump, Waters 2414 RI detector and columns: Styragel, HT 3, HT 4. The calibration was performed with commercial polystyrene standards. Tetrahydrofuran (THF) was used as the mobile phase at a flow rate of 0.8 mL min^{-1} at 30 °C. The refractive-index increment (dn/dc) was determined with a Wyatt Optilab DSP differential refractometer at 690 nm.

Differential scanning calorimetry (DSC) measurements were performed on a TA Q100 apparatus. The samples were heated from 0 to 100 °C, held for 2 min to erase the thermal history, then cooled to 0 °C at a rate of 20 °C min^{-1}, and finally heated to 100 °C at a rate of 10 °C min^{-1}.

The hydrodynamic diameter and size distribution of micelles were determined by dynamic light scattering (DLS) at 90°



SCHEME 1 Synthetic route of amphiphilic $A_{14}B_7$ multimiktoarm star copolymers base on β-CD.

angle to the incident beam and at 25 °C on a Brookhaven 90 Plus particle size analyzer. All micelle solutions measured by DLS had a polymer concentration of 0.3 mg/mL.

TEM images were obtained using JEM-1230 operating at an acceleration voltage of 60 kV. A drop of 0.3 mg/mL micelle solution was placed onto the surface of Formvar-carbon film-coated copper grids. Excess solution was quickly wicked away with a filter paper. All grids were finally negatively stained by 2 wt % phosphotungstic acid.

AFM samples were prepared through drop-casting of the micelle solution (0.3 mg/mL) onto the freshly cleaved mica and dried at room temperature for 48 h. AFM (tapping mode) was operated on a Seiko SPI3800*N* station (Seiko Instruments). Silicon tips (NSG10, NT-MDT) with a resonance frequency of ~330 KHz were used.

The critical micelle concentration (CMC) was determined by fluorescence measurement using pyrene as a fluorescent probe. Fluorescence excitation spectra were recorded on HI-

TACHI F-4500 fluorescence spectrometer at 390 nm emission wavelength and 2.5 nm slit width. The pyrene concentration in the solution was chosen to be 6.0×10^{-7} M.

Synthesis of Per-6-(*tert*-butyldimethylsilyl)-*β*-CD (Scheme 1; CD-Core)

Per-6-(*tert*-butyldimethylsilyl)-*β*-CD was synthesized according to the procedure described in the literature[65] as follows: dry *β*-CD (2.27 g, 2 mmol) was dissolved under vigorous stirring in 50 mL anhydrous pyridine cooled in an ice bath. *tert*-Butylchlorodimethylsilane (TBDMSCl) (2.40 g, 16 mmol) dissolved in 20 mL anhydrous pyridine was then added dropwise into the cooled reaction vessel over 30 min. The reaction mixture was stirred for 18 h under argon atmosphere at room temperature, and then the solvent was removed under reduced pressure to give a white solid, which was taken up in chloroform and washed successively with $KHSO_4$ (100 mL, 1 M) and water. The organic phase was dried over magnesium sulfate, filtered, and evaporated to dryness. Yield: 3.10g (90%). MS for $C_{84}H_{168}O_{35}Si_7$: m/z = 1958 $(M+Na)^+$.

^{1}H NMR ($CDCl_3$, 500MHz): 0.03 (s, 21H, CH_3-Si), 0.04 (s, 21H, CH_3-Si), 0.89 (s, 63H, $(CH_3)_3C$), 3.55 (d, 7H, H-6a)′3.62 (m, 14H, H-2; H-5), 3.72 (d, 7H, H-3), 3.89 (d, 7H, H-6b) 4.03 (d, 7H, H-4), 4.89(d, 7H, H-1).

Synthesis of Cyclodextrin-Centered 14-Arm Star Poly(ε-caprolactone)s (CDSi-SPCL) by Controlled Ring-Opening Polymerization (Scheme 1)

CDSi-SPCL was synthesized by controlled ring-opening polymerization of ε-CL using per-6-(*tert*-butyldimethylsilyl)-*β*-CD (CD-Core) as the multifunctional initiator in the presence of $Sn(Oct)_2$. A typical polymerization procedure was as follows: per-6-(*tert*-butyldimethylsilyl)-*β*-CD (0.773 g, 5.6 mmol of OH group) was dried at 70 °C under reduced pressure overnight and transferred into a flamed-dried ampoule. Then, CL (3.88 g, 34 mmol) and a magnetic stirring bar were added to the ampoule under argon atmosphere. After CD-Core was dissolved in CL completely, the tube was then connected to a schlenkline, where an exhausting-refilling process was repeated three times. 20 mg $Sn(Oct)_2$ in 1 mL dry toluene was added to the mixture, and the exhausting-refilling process was carried out again to remove the toluene. The ampoule was put into an oil bath at 125 °C for 24 h bulk polymerization. The crude polymer was dissolved in THF and poured into excess methanol to precipitate the product, which was dried in vacuum to constant weight. Yield: 4.58g (98%).

Synthesis of Cyclodextrin-Centered 14-Arm Star ω-Acetyl-Poly(ε-caprolactone)s (Scheme 1, CDSi-ACSPCL)

The hydroxyl end groups of the CDSi-SPCL were blocked by acetic chloride. A typical procedure was as follows: CDSi-SPCL95 (3.0 g, 3.28 mmol of OH group) and triethylamine (TEA) (0.98 g, 9.8 mmol, 1.34 mL) were dissolved in 100 mL dry THF. The solution was cooled to 0 °C, and acetic chloride (0.77 g, 9.8 mmol, 0.7 mL) in 10 mL dry THF was added dropwise to the vigorously stirred solution over 30 min. Thereafter, the reaction mixture was stirred at room temperature for 24 h. The precipitated byproduct was removed by filtration, and the solution was evaporated to dryness. The crude product was dissolved in 50 mL methylene chloride, and then the organic phase was washed successively with 1 M $NaHCO_3$ aqueous solution and 80 mL water and finally dried over anhydrous $MgSO_4$. The concentrated solution was poured into cold diethyl ether to precipitate the product. The resulting white solid was dried in vacuum at room temperature for 24 h. Yield: 2.4 g (80% for polymer weight).

Desilylation of CDSi-ACSPCL (Scheme 1)

The primary hydroxyl groups on the cyclodextrin-core were recovered by desilylation of the *tert*-butyldimethylsilyl ether groups in the presence of $BF_3{\cdot}Et_2O$. A typical procedure was as follows: $BF_3{\cdot}Et_2O$ (0.5 mL, 2 mmol) in 10 mL anhydrous CH_2Cl_2 was added dropwise to a solution of CDSi-ACSPCL95 (2.0 g, 1.04 mmol of *tert*-butyldimethylsilyl group) in 80 mL anhydrous CH_2Cl_2 under stirring. The reaction mixture was stirred for 12 h under argon atmosphere at room temperature and then washed successively with $NaHCO_3$ (100 mL, 1 M) and water. The organic phase was dried over anhydrous $MgSO_4$. The concentrated solution was poured into cold methanol to precipitate the product. The resulting white solid (denoted as CD-ACSPCL, Scheme 1) was dried in vacuum at room temperature for 24 h. Yield: 1.7 g (90% for polymer weight).

Synthesis of CD-ACSPCL-Br Macroinitiator for ATRP (Scheme 1)

A typical procedure was as follows: CD-ACSPCL95 (1.4 g, 0.78 mmol of OH group) was dissolved in 40 mL anhydrous THF, followed by the introduction of triethylamine (TEA) (0.79 g, 7.8 mmol, 1.1 mL) via a syringe. 2-Bromisobutyryl bromide (1.80 g, 7.8 mmol, 1.0 mL) in 5 mL anhydrous THF was added dropwise to the vigorously stirred solution at 0 °C over 30 min. The reaction mixture was stirred at room temperature overnight. The precipitated byproduct was removed by filtration, and the solution was evaporated to dryness. The crude product was dissolved in 40 mL methylene chloride, and then washed successively with 1 M $NaHCO_3$ aqueous solution and 40 mL water, and finally dried over anhydrous $MgSO_4$. The concentrated solution was poured into methanol to precipitate the product. The resulting white solid was dried in vacuum at room temperature for 24 h. Yield: 1.14 g (75% for polymer weight).

Synthesis of $A_{14}B_7$ Multimiktoarm Star Copolymers of CDS(PCL-P*t*BA) by ATRP (Scheme 1)

In a typical produce, CD-ACSPCL95-Br (400 mg, 0.21 mmol of Br group) and CuBr (30 mg, 0.21 mmol) were charged into a previously flame-dried ampoule filled with argon. The ampoule was degassed and backfilled with argon three times. Deoxygenated toluene (18 mL) and PMDETA (36 mg, 0.21 mmol) were added via a syringe, and the solution was stirred for 5 min. Finally, *t*BA (2.56 g, 21 mmol) was added. The reaction mixture was degassed with three freeze-pump-thaw cycles, left in argon, and placed in an oil bath at 70 °C for 240 min. Subsequently, the polymerization mixture was diluted with THF, passed through an alumina column to

TABLE 1 Characterization of Cyclodextrin-Centered 14-Arm Star PCL Homopolymers[a]

Sample[b]	$[CL]_0/[CD\text{-}Core]$ (Molar Ratio)	Conv (%)[c]	$M_{n,Cal}$ (g mol^{-1})[d]	$M_{n,NMR}$ (g mol^{-1})[e]	$M_{n,MALLS}$ (g mol^{-1})[f]	$M_{n,SEC}$ (g mol^{-1})[g]	PDI[g]	N_{PCL}[h]
CDSi-SPCL95	85	98.2	11,500	12,800	13,800	14,200	1.13	6.8
CDSi-SPCL185	185	97.5	22,500	23,000	24,400	25,300	1.26	13.2
CDSi-SPCL265	255	98.9	30,700	32,100	31,500	36,300	1.15	18.9

[a] Polymerization conditions: bulk, 125 °C, 24 h.
[b] CDSi-SPCL95, 95 represents the average CL repeat units of one CDSi-SPCL macromolecule determined by ^{1}H NMR.
[c] Conversion was calculated on the basis of gravimetric method.
[d] Calculated from the equation: $M_{n,Cal} = ([CL]_0/[CD\text{-}Core]) \times 114 \times$ Conversion (%) $+ M_{CD\text{-}Core}$.
[e] This calculation is based on the integration of the CL units as compared to that of the *tert*-butyl protons of the CD-Core: $M_{n,NMR} = (\frac{I_b}{2}) \times (\frac{9\times7}{I_a}) \times 114 + M_{CD-core}$ (see Figure 1).
[f] Measured by connecting a multi-angle laser light scattering detector to the SEC.
[g] Determined by SEC analysis with polystyrene standards.
[h] The average number of CL units in each arm of the 14-arm star PCL homopolymers, calculated from the ^{1}H NMR.

remove the catalyst. The polymer was recovered by precipitation into cold hexane and dried in vacuum. Yield: 1.22 g (31.9%).

Synthesis of Amphiphilic $A_{14}B_7$ Multimiktoarm Star Copolymers of CDS(PCL-PAA) by Selective Hydrolysis (Scheme 1)s

A typical example is given below. To a methylene chloride solution of CDS(PCL95-P*t*BA248) (200 mg), trifluoroacetic acid (1 mL) was added dropwise under stirring. The mixture was kept at 30 °C for 72 h. After the solvent was evaporated in vacuum, the product was dissolved in THF and precipitated in cold hexane. Yield: 110 mg (79% for polymer weight).

Micellization of CDS(PCL-PAA)

At ambient temperature around 25 °C, 25 mg of CDS(PCL-PAA) sample was dissolved in 10 mL DMF, and then distilled water (~10 mL) was added dropwise to the solution under vigorous stirring. The solution was stirred for 2 h and dialyzed against distilled water over 48 h to remove DMF. The final concentration of the micelle solution was 1.0 mg/mL.

RESULTS AND DISCUSSION

Synthesis of Per-6-(*tert*-butyldimethylsilyl)-*β*-CD (CD-Core)

The synthesis of per-6-(*tert*-butyldimethylsilyl)-*β*-CD as a multifunctional initiator was based on the following two facts: first, only the 7 primary hydroxyl groups of *β*-CD can be silylated by *tert*-butylchlorodimethylsilane due to the inactivity of the hindered 14 secondary hydroxyl groups. *tert*-Butyldimethylsilyl ether group is stable to most reaction conditions and can be removed under specific mild conditions, which provides a convenient way to design the initiator from *β*-CD for the synthesis of $A_{14}B_7$ multimiktoarm star copolymers in the next steps; second, because of the strong intra and inter molecular hydrogen bonds, *β*-CD shows poor solubility in *ε*-caprolactone (CL), the incorporating of seven *tert*-butyldimethylsilyl ether groups onto *β*-CD would reduce the hydrogen bonds and increase its solubility in CL, which permits the simultaneous initiating of all the 14 secondary hydroxyl groups for the controlled ring-opening polymerization of CL.

The structure of per-6-(*tert*-butyldimethylsilyl)-*β*-CD was confirmed by ^{1}H NMR and MS (see Supporting Information Fig. S1).

Synthesis of Cyclodextrin-Centered 14-Arm Star Poly(*ε*-caprolactone)s (CDSi-SPCL) by Controlled Ring-Opening Polymerization

The synthesis of CDSi-SPCL was carried out by the controlled ring-opening bulk polymerization of CL using per-6-(*tert*-butyldimethylsilyl)-*β*-CD as a multifunctional initiator and $Sn(Oct)_2$ as the catalyst at 125 °C as shown in Scheme 1. Three different monomer/initiator ratios were utilized to achieve CDSi-SPCL with various polymerization degrees. Detailed characterization results are summarized in Table 1.

$$N_{PtBA} = (I_c + I_g - I_f) \times \frac{2}{I_f} \times N_{PCL} \quad (1)$$

where N_{PtBA} is the average number of *t*BA units in each arm (see Table 2), and I_f, I_c, I_g represent the integral area of the signals at 4.0 ppm (H^f), 2.29 ppm (H^c) and 2.2 ppm (H^g) due to the protons of the PCL and P*t*BA block.

Figure 1 exhibits a representative ^{1}H NMR spectrum of CDSi-SPCL (CDSi-SPCL265). It clearly shows that besides the major proton signals of PCL chains (H^{c-f}), there are additional signals of the per-6-(*tert*-butyldimethylsilyl)-*β*-CD core moiety, that is, signals corresponding to methyl protons (H^b) and *tert*-butyl protons (H^a) of the *tert*-butyldimethylsilyl ether groups. The triplet at 3.65 ppm (H^g) is assigned to the PCL methylene protons conjoint with the hydroxyl end groups. The number average molecular weight of the CDSi-SPCL ($M_{n,NMR}$) can be calculated by the integration of signals at 4.05 ppm (H^f) of the CL repeat units and that of signals at 0.89 ppm (H^a) of the *tert*-butyldimethylsilyl ether groups (see Table 1). Notably, the actual molecular weights of CDSi-SPCL obtained from ^{1}H NMR spectra are close to the values calculated by observed conversion and $[CL]_0/[CD\text{-core}]$,

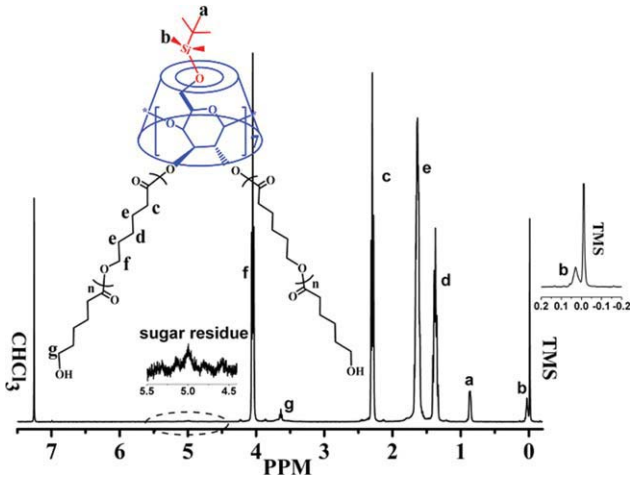


FIGURE 1 ^{1}H NMR spectrum (500MHz) of CDSi-SPCL265 in $CDCl_3$. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

which verifies the well-defined architectures of these samples.

SEC traces (Fig. 2) reveal unimodal elution peaks with reasonably narrow polydispersity ($\leq$1.26), although slight tailing was detected in the low-molecular-weight region, which was attributed to unavoidable chain transfer side reactions during the polymerization. The results of the actual molar masses of CDSi-SPCL measured by SEC-MALLS have confirmed the values obtained from ^{1}H NMR (Table 1), which demonstrates that CDSi-SPCL with designed architectures have been successfully prepared.

Synthesis of Cyclodextrin-Centered 14-Arm Star ω-Acetyl-Poly(ε-caprolactone)s (CDSi-ACSPCL)

The 14-arm star poly(ε-caprolactone) (CDSi-SPCL) contains reactive hydroxyl end groups which can also react with 2-bromisobutyryl bromide in the next step, it will interfere with the designed synthetic route of $A_{14}B_7$ multimiktoarm star copolymers. Thus, acetyl chloride was used to block the hydroxyl end groups of CDSi-SPCL. From the ^{1}H NMR spectrum shown in Figure 3, it is obvious that the signal of the methylene protons of PCL conjoint with hydroxyl end groups [Fig. 1 (H^g)] disappeared completely, whereas a new signal corresponding to methyl protons of acetyl group appeared at 2.03 ppm. Moreover, integral ratio of H^f and H^h is in well agreement with the theoretical value, suggesting that the hydroxyl groups of CDSi-SPCL have been completely blocked.

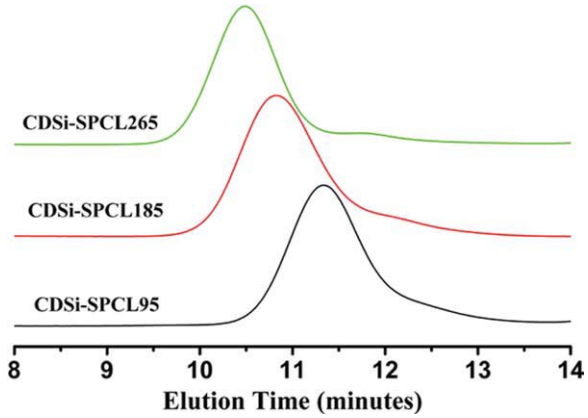


FIGURE 2 SEC traces of cyclodextrin-centered 14-arm star PCL homopolymers. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

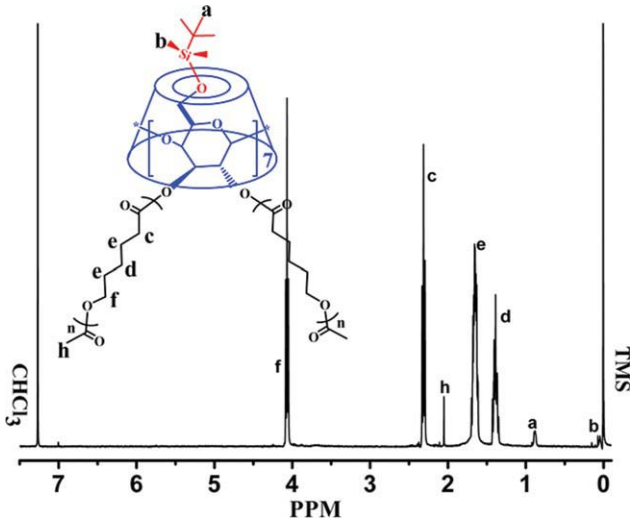


FIGURE 3 ^{1}H NMR spectrum (500MHz) of CDSi-ACSPCL265 in $CDCl_3$. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Desilylation of the Cyclodextrin-Centered 14-Arm Star ω-Acetyl-Poly(ε-caprolactone)s

The *tert*-butyldimethylsilyl ether group is widely used for hydroxyl protection which can be completely removed in the presence of fluoride ion or aqueous acid. Here, boron trifluoride diethyl etherate ($BF_3{\cdot}Et_2O$) was used to desilylate the *tert*-butyldimethylsilyl ether groups. The ^{1}H NMR spectrum of a representative desilylated CDSi-SPCL (denoted as CD-ACSPCL265) is shown in Figure 4. After desilylation, only the signals at 0.04 ppm (H^b) and 0.89 ppm (H^a) assigned to the protons of the *tert*-butyldimethylsilyl ether groups disappeared, other signals assigned to the protons of PCL chains remained intact, indicating that the seven primary hydroxyl groups on the β-CD core moiety have been recovered, and there were no degradation of the PCL chains occurred.

Synthesis of CD-ACSPCL-Br Macroinitiator for ATRP

To introduce seven hetero arms onto the presynthesized 14-arm star poly(ε-caprolactone) (CD-ACSPCL), the hydroxyl groups on the β-CD core moiety were functionalized with 2-bromoisobutyryl bromide, which is a convenient initiator for the ATRP of acrylate monomers. Considering the steric hindrance of the seven primary hydroxyl groups, large excess of 2-bromoisobutyryl bromide was used to ensure all the hydroxyl groups could be capped. The ^{1}H NMR spectrum of

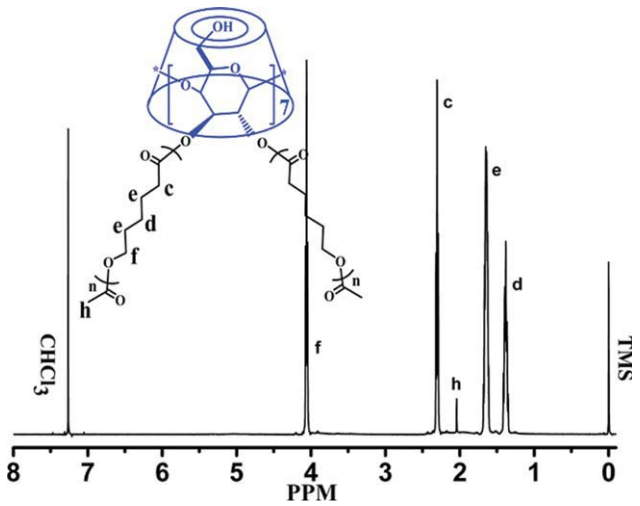


FIGURE 4 ^{1}H NMR spectrum (500MHz) of CD-ACSPCL265 in $CDCl_3$. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

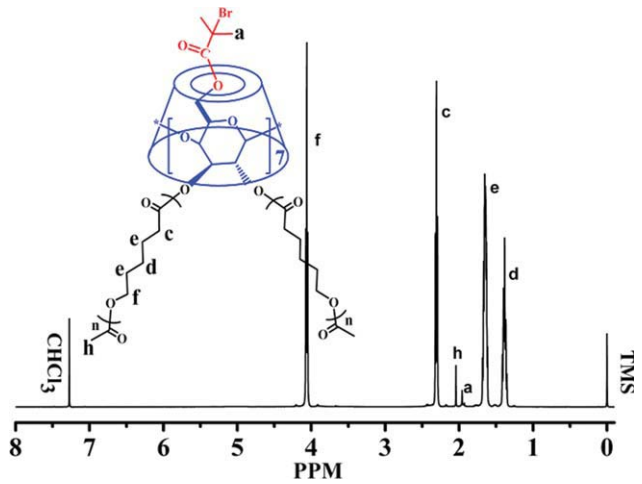


FIGURE 5 ^{1}H NMR spectrum (500MHz) of CD-ACSPCL265-Br in $CDCl_3$. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

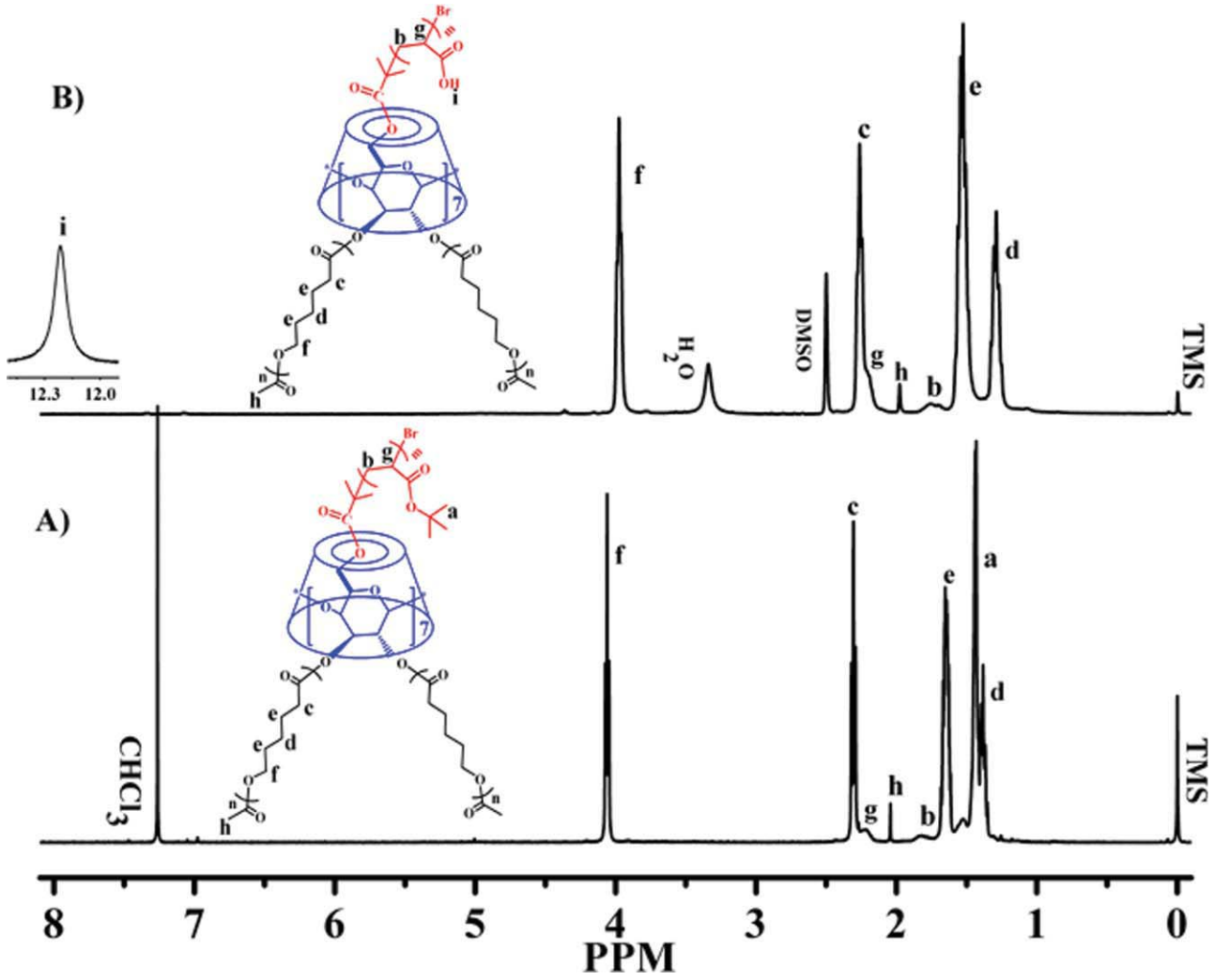


FIGURE 6 ^{1}H NMR spectra (500MHz) of CDS(PCL265-P*t*BA133) (A) in $CDCl_3$ and CDS(PCL265-PAA133) (B) in DMSO-D_6. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE 2 Characterization of the $A_{14}B_7$ Multimiktoarm Star Copolymers [CDS(PCL-P*t*BA)][a]

Sample[b]	Macroinitiator	Time (min)	Conv (%)[c]	$M_{n,Cal}$ (g mol^{-1})[d]	$M_{n,NMR}$ (g mol^{-1})[e]	$M_{n,SEC}$ (g mol^{-1})[f]	PDI[f]	N_{PtBA}[g]
CDS(PCL95-P*t*BA248)	CD-ACSPCL95-Br	240	31.9	41,400	44,600	31,800[h]	1.12	35.4
CDS(PCL95-P*t*BA333)	CD-ACSPCL95-Br	300	44.3	52,500	55,400	35,400	1.13	47.6
CDS(PCL185-P*t*BA93)	CD-ACSPCL185-Br	180	12.1	33,800	34,900	28,200	1.10	13.3
CDS(PCL265-P*t*BA133)	CD-ACSPCL265-Br	180	16.4	46,800	49,100	46,300	1.19	19.0
CDS(PCL265-P*t*BA442)	CD-ACSPCL265-Br	360	58.5	84,500	88,700	80,700	1.34	63.1

[a] Polymerization conditions: toluene, $[tBA]_0$ =1.0 mol/L, 70 °C, $[tBA]_0$/[CD-ACSPCL-Br]$_0$/CuBr/PMDETA = 100:1:1:1, where $[tBA]_0$, [CD-ACSPCL-Br]$_0$ represent initial concentrations of *t*BA and initiation sites on CD-ACSPCL-Br macroinitiator, respectively.
[b] CDS(PCL95-P*t*BA248), 95 and 248 represents the average CL and *t*BA repeat units of one CDS(PCL-P*t*BA) macromolecule, respectively, determined by ^{1}H NMR.
[c] Conversion was calculated on the basis of gravimetric method.
[d] Calculated from the equation: $M_{n,Cal} = ([tBA]_0/[\text{CD-ACSPCL-Br}]_0) \times 128 \times$ Conversion (%)+$M_{\text{CD-ACSPCL-Br}}$, where $[tBA]_0/[\text{CD-ACSPCL-Br}]_0$ equals 100.
[e] Calculated from ^{1}H NMR spectra of the miktoarm star copolymers as follows: $M_{n,NMR} = (I_c + I_g - I_f) \times \frac{2}{f} \times N_{PCL} \times 128 + M_{CD-ACSPCL-Br}$ (see Figure 6A).
[f] Determined by SEC analysis with polystyrene standards.
[g] The average number of *t*BA units in each arm of the $A_{14}B_7$ multimiktoarm star copolymers, calculated from the ^{1}H NMR.
[h] $M_{w,MALLS}$ = 48,100, $M_{n,MALLS}$ = 42,900.

the functionalized macroinitiator CD-ACSPCL265-Br was presented in Figure 5. After esterification, new signals corresponding to methyl protons (H^a) of the bromo ester group appeared at 1.92 ppm, and the ratio of peak areas of H^a and H^h (I^a/I^h) is 0.91, which is close to the theoretical value (1.0). It is therefore demonstrated that nearly all the primary hydroxyl groups on the β-CD core moiety of CD-ACSPCL have been substituted with the bromo ester groups. In addition, the integral values of the PCL arms are not changed, suggesting that no hydrolysis of the PCL arms occurred.

Synthesis of $A_{14}B_7$ Multimiktoarm Star Copolymers of CDS(PCL-P*t*BA) by ATRP

The macroinitiator CD-ACSPCL-Br was used for the copper(I)-mediated ATRP of *tert*-butyl acrylate (*t*BA) to produce $A_{14}B_7$ multimiktoarm star copolymers in conjunction with PMDETA as a ligand. Previously, Gnanou and coworkers[66] reported the controlled polymerization of *tert*-butyl acrylate (*t*BA) by ATRP from an octafunctional initiator and found that although the star-star coupling was not obvious compared with styrene polymerization, low monomer conversions were still needed. Likewise, some other groups also reported that well-defined star P*t*BA prepared by ATRP should take care of the polymerization conditions such as reaction temperature, reagent concentrations, and monomer conversions to minimize intermolecular star-star coupling reactions.[67,68] Therefore, in this article, all polymerization were conducted in toluene under optimized conditions: $[tBA]_0$ = 1.0 mol/L, 70 °C, $[tBA]_0$/[CD-ACSPCL-Br]$_0$/CuBr/PMDETA = 100:1:1:1. where $[tBA]_0$,[CD-ACSPCL-Br]$_0$ represent initial concentrations of *t*BA and initiation sites on CD-ACSPCL-Br macroinitiator, respectively. Relatively low monomer conversions were kept to decrease intermolecular coupling reactions and the lengths of the P*t*BA blocks were varied through terminating the polymerizations at different time intervals. Table 2 summarizes the results of these polymerizations. The ^{1}H NMR spectrum of a representative $A_{14}B_7$ multimiktoarm star copolymer [CDS(PCL265-P*t*BA133)] is shown in Figure 6(A). All the expected peaks attributed to the PCL and P*t*BA block can be clearly detected. The polymerization degree of P*t*BA arms can be calculated by eq 1:

Figure 7 shows the SEC traces of the $A_{14}B_7$ multimiktoarm star copolymers [CDS(PCL-P*t*BA)] in comparison with those of the original 14-arm star PCL homopolymer precursors. It reveals that, after ATRP of *t*BA, all the SEC traces shift to the higher molar mass region. When the *t*BA monomer conversion was below 45%, symmetrical unimodal elution peaks with narrow molecular weight distributions (<1.20) were observed, indicating the successful synthesis of the CDS(PCL-P*t*BA) with well-defined structure. However, when the monomer conversion of *t*BA reached 58.5% [CDS(PCL265-P*t*BA442)], the PDI value of the obtained miktoarm star copolymer increased to 1.34, which was tentatively attributed to a small amount of coupling reactions between the star copolymers in ATRP process. To further confirm the architecture of the $A_{14}B_7$ multimiktoarm star copolymer, actual molar mass of one sample [CDS(PCL95-P*t*BA248), Table 2] was measured by SEC-MALLS. The $M_{n,MALLS}$ of CDS(PCL95-P*t*BA248) was 42,900, which was close to the value calculated from the ^{1}H NMR ($M_{n,NMR}$ = 44,600), indicating the sample prepared possesses the designed $A_{14}B_7$ structure. It should be pointed out that some of the miktoarm star copolymers showed more symmetrical SEC traces with lower PDIs compared with those of the corresponding star homopolymer precursors. These observations may be attributed to the fact that a small fraction of star PCL homopolymers with low molecular weight have been removed by repeated precipitations during the synthesis process of CD-ACSPCL-Br macroinitiator.

Thermal and Crystallization Behaviors of 14-Arm Star Poly(ε-caprolactone)s (CDSi-SPCL) and $A_{14}B_7$ Multimiktoarm Star Copolymers [CDS(PCL-P*t*BA)]

The thermal and crystallization behaviors of CDSi-SPCL homopolymers and CDS(PCL-P*t*BA) miktoarm star copolymers were investigated by DSC as shown in Figure 8. In the case of CDSi-SPCL homopolymers, both melting temperature (T_m) and crystallization temperature (T_c) increase with the

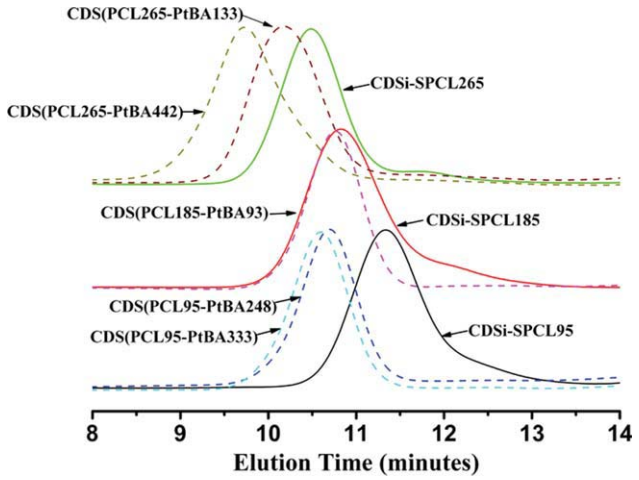


FIGURE 7 SEC traces of $A_{14}B_7$ multimiktoarm star copolymers and their precursors. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

increasing molecular weight. As for miktoarm star copolymers CDS(PCL-P*t*BA), T_m for PCL segment ($T_{m,PCL}$) could be detected when the molecular weight of PCL segment is high enough [CDS(PCL185-P*t*BA93), CDS(PCL265-P*t*BA133), CDS(PCL265-P*t*BA442)] and the values of the $T_{m,PCL}$ and $T_{c,PCL}$ are lower than that of the corresponding CDSi-SPCL precursors. Moreover, not any T_g trace for the P*t*BA segment is observed. For the samples with the same molecular weight of PCL segment [CDS(PCL265-P*t*BA133) and CDS(PCL265-P*t*BA442)], both $T_{m,PCL}$ and $T_{c,PCL}$ decrease with the increasing arm length of P*t*BA segment. These observations clearly indicate that in $A_{14}B_7$ multimiktoarm star copolymers, amorphous P*t*BA segment highly hinders the crystalline process of the PCL segment and short PCL segment and P*t*BA segment are miscible. However, long PCL segment display strong crystallization ability, leading to individual T_m and T_c.

Synthesis of Amphiphilic $A_{14}B_7$ Miktoarm Star Copolymers of CDS(PCL-PAA) by Selective Hydrolysis

The *tert*-butyl groups of the P*t*BA block were converted into carboxyl groups by selective hydrolysis with excess of trifluoroacetic acid in dichloromethane to form PAA block[69] (Scheme 1). It has earlier been shown that to avoid degradation of the polyester, short reaction time at ambient temperature can cleave off the isobutene moieties from P*t*BA block completely.[70] Nevertheless, in our work, it is observed that only 70% of the *tert*-butyl groups had been converted to carboxyl form at room temperature for 12 h. This may due to the fact that the decreasing solubility of the amphiphilic copolymers in dichloromethane led to some precipitation in the course of the reaction, making the remained *tert*-butyl groups inaccessible for hydrolysis. Therefore, complete hydrolysis of the *tert*-butyl groups had been achieved by increasing the temperature to 30 °C and prolonging the reaction time to 72 h. Figure 6(B) shows the ^{1}H NMR spectrum of the amphiphilic $A_{14}B_7$ multimiktoarm star copolymer CDS(PCL265-PAA133). Compared with the ^{1}H NMR spectrum

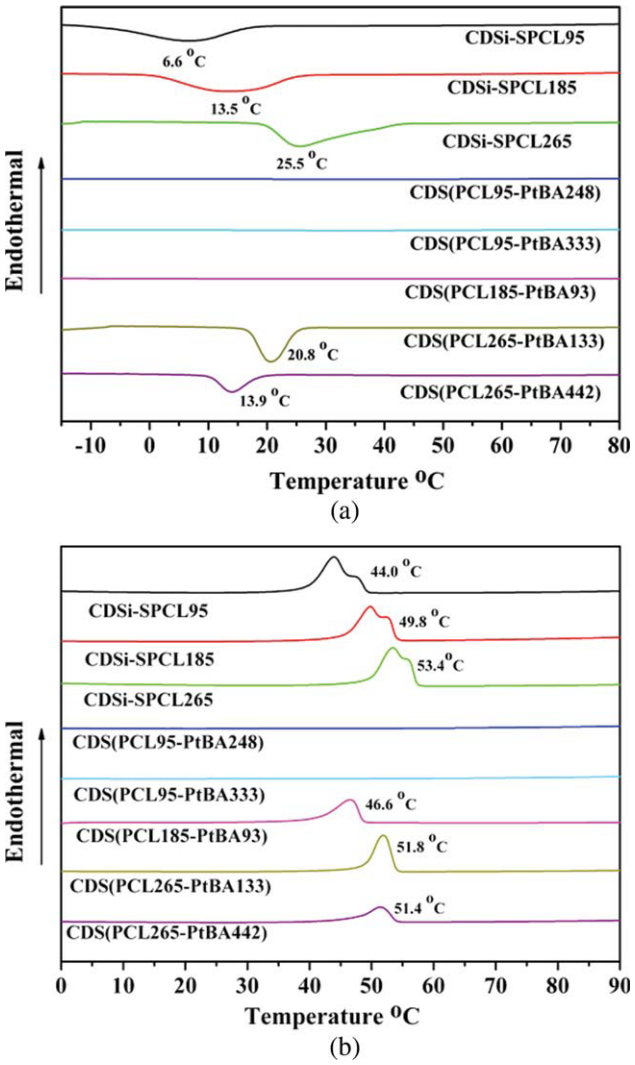


FIGURE 8 DSC curves of CDSi-SPCL homopolymers and CDS(PCL-P*t*BA) miktoarm star copolymers in the cooling run (a) and the second heating run (b). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE 3 Characterization of the Amphiphilic $A_{14}B_7$ Miktoarm Star Copolymers [CDS(PCL-PAA)] Micelles by DLS

Sample	Weight Fraction of PAA (%)	Particle Size (nm)[a]	PDI[b]	CMC (mg L^{-1})
CDS(PCL95-PAA248)	58.3	15.6	0.254	1.73
CDS(PCL95-PAA333)	65.3	11.2	0.218	2.34
CDS(PCL185-PAA93)	22.5	123.7	0.238	0.54
CDS(PCL265-PAA133)	22.9	117.3	0.205	0.56
CDS(PCL265-PAA442)	49.8	40.2	0.265	0.74

[a] Number-average mean diameters measured by dynamic light scattering (DLS).
[b] PDI denotes the polydispersities of nanoparticles in aqueous solution.

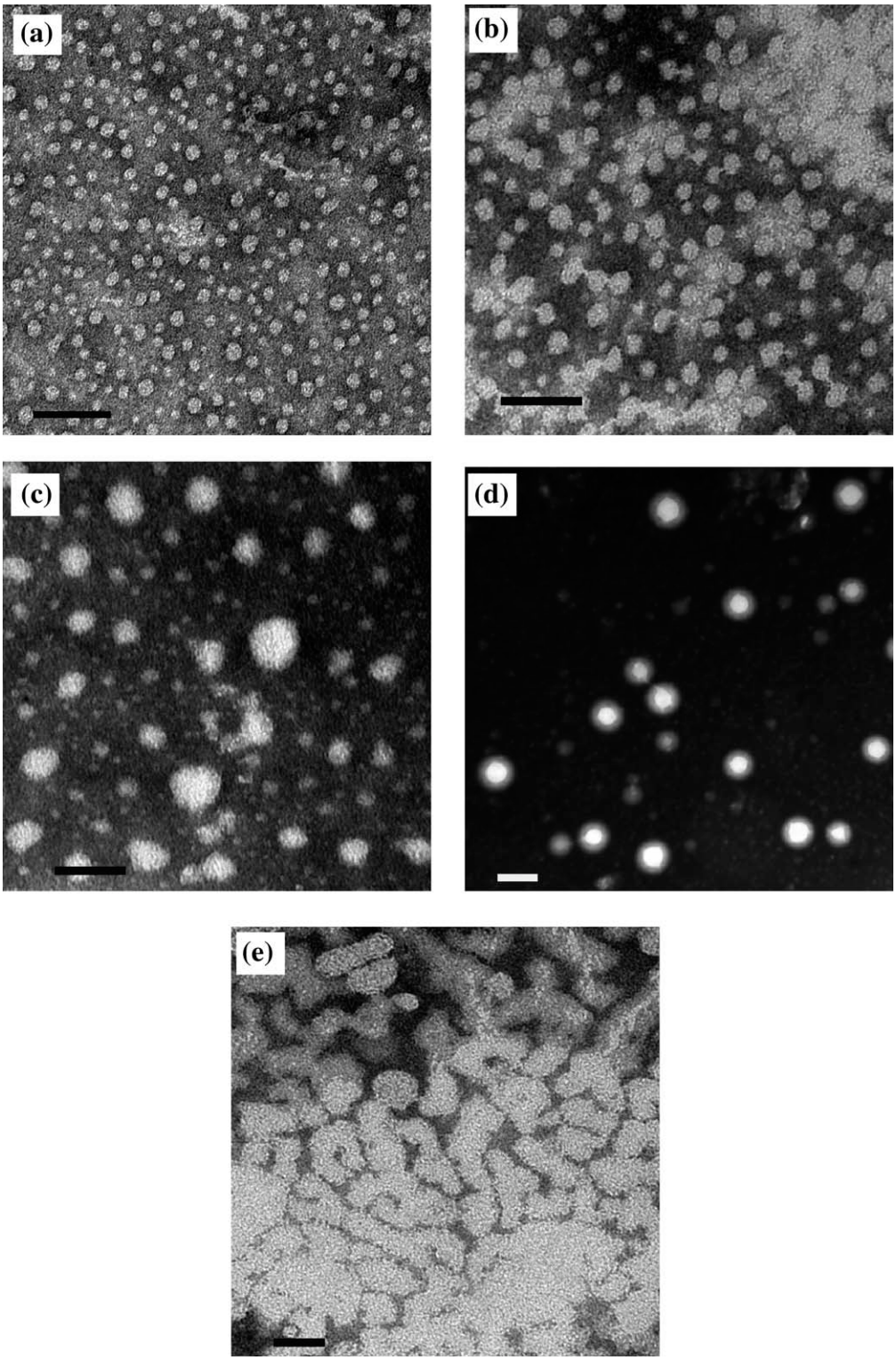


FIGURE 9 TEM micrography of aggregates from (a) CDS(PCL95-PAA333), (b) CDS(PCL95-PAA248), (c) CDS(PCL265-PAA442), (d) CDS(PCL265-PAA133), (e) CDS(PCL185-PAA93). The scale bar in (a) (b) (c) represents 100 nm and in (d) (e) represents 200 nm.

of CDS(PCL265-P*t*BA133) in Figure 6(A), signal at 1.4 ppm assigned to *tert*-butyl protons (H^a) has completely disappeared and a new signal corresponding to acid proton (H^i) appears at 12.7 ppm, indicating the removal of the *tert*-butyl groups. In addition, the major proton signals of PCL chains ($H^{c,d,e,f}$) remained essentially intact, which suggests the successful synthesis of the amphiphilic $A_{14}B_7$ multimiktoarm star copolymer without any hydrolysis of PCL segments.

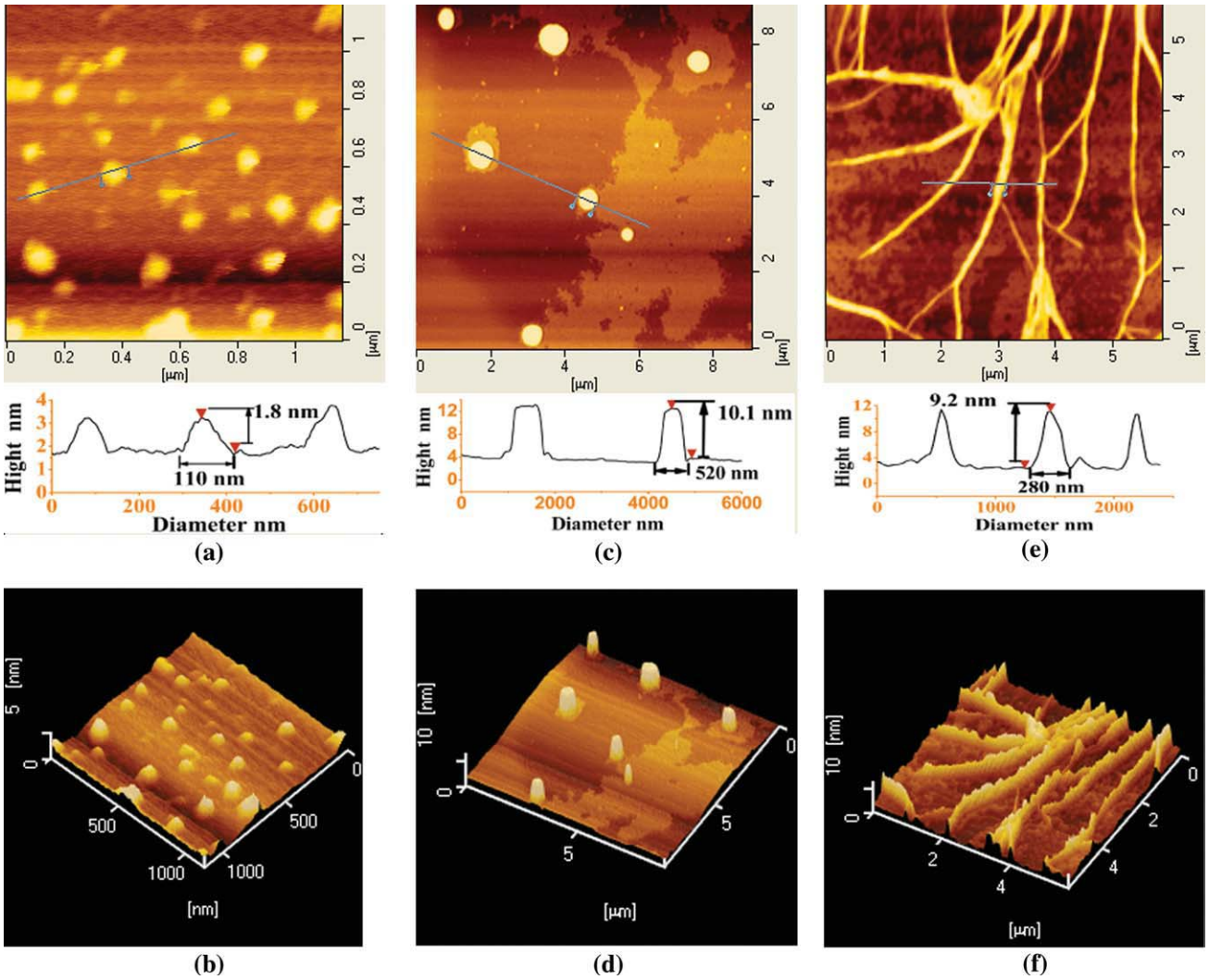


FIGURE 10 TM-AFM height images of (a) and (b) CDS(PCL95-PAA248), (c) and (d) CDS(PCL265-PAA133), (e) and (f) CDS(PCL185-PAA93). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Self-Assembly Behaviors of Amphiphilic $A_{14}B_7$ Multimiktoarm Star Copolymers of CDS(PCL-PAA)

These synthesized $A_{14}B_7$ multimiktoarm star copolymers possess an amphiphilic structure consisting of hydrophobic PCL segment and hydrophilic PAA segment, which can form aggregates sin aqueous solution. The critical micelle concentration (CMC) of amphiphilic copolymer was usually measured by fluorescence technique using pyrene as a probe.[71] Pyrene will preferentially incorporate into hydrophobic microdomains showing strong fluorescence intensity while weak fluorescence intensity and a shift of excitation peak in a polar environment (aqueous solution). In addition, the sharp rise in intensity ratio of peaks at 338 and 333 nm of pyrene in the excitation spectra indicates the on-set of micellization (CMC) for amphiphilic copolymers (Supporting Information, Fig. S2). The CMC value of these amphiphilic miktoarm star copolymers was relatively low (ranging from 0.54 mg/L to 2.34 mg/L), increasing as the weight fraction of PAA increased, as shown in Table 3, which was probably due to the multimiktoarm star architecture. These results indicate that the aggregates in the aqueous solution are thermodynamically stable which can be further used as potential nanocarriers.

The morphologies of the self-assembled aggregates from these amphiphilic $A_{14}B_7$ multimiktoarm star copolymers were investigated by DLS and TEM as shown in Figure 9 and Table 3. Nearly spherical micelles with number average mean diameters from 10 to 50 nm were observed when the weight fraction of PAA segment was ranging from 65.3% to 49.8% for CDS(PCL95-PAA333), CDS(PCL95-PAA248) and CDS(PCL265-PAA442). The micelle diameters increased as the decreasing of the weight fraction of hydrophilic PAA block. However, with further decreasing the weight fraction of PAA block to 22.9% within CDS(PCL265-PAA133) sample, large micelles with an average diameter more than 120 nm were observed. These observations are attributed to the fact that short hydrophilic PAA blocks could not evade the

hydrophobic interaction and van der Waals interaction between exposed hydrophobic PCL domains, and the copolymers prefer to form large aggregates to balance these interactions. Nevertheless, in the case of CDS(PCL185-PAA93) having a similar PAA weight fraction (22.5%) compared with CDS(PCL265-PAA133), wormlike aggregates were observed. It should be noted that the sizes of these wormlike aggregates measured by DLS are not in accordance with the TEM results (Table 3), which is attributed to that the basic equations to calculate the hydrodynamic diameter in DLS measurement are originated from the correlation function cumulant analysis based on the assumption that the particles are noninteracting spheres and not anisotropic objects.[72] From these results, we could conclude that both the architecture of the copolymers and the hydrophilic PAA composition influence the morphology and dimension of the self-assembled aggregates. However, the influence of the $A_{14}B_7$ miktoarm star architecture on the morphology of the aggregates is still unclear, which is deserved to be investigated in the near future.

To further study the self-assembled morphologies of these amphiphilic miktoarm star copolymers, tapping-mode atomic force microscopy (TM-AFM) was used to observe the dry state of the aggregates on mica surfaces. The copolymers were drop-cast from water with the concentration of 0.3 mg/mL and dried onto mica surfaces at room temperature for 48 h. Figure 10 shows the TM-AFM height images of CDS(PCL-PAA) with different compositions. Generally speaking, the morphologies of these aggregates observed by TM-AFM were comparable with TEM results, but the dimensions were not. For CDS(PCL95-PAA248), flat circular structures with an average diameter of 100 nm was visualized [Fig. 10(a,b)], which was significantly larger than the TEM and DLS results (~15 nm). However, the measured average height of these micelles in dry state was less than 2 nm, indicating a highly collapsed structure. As for CDS(PCL265-PAA133) and CDS(PCL185-PAA93), disklike structure [Fig. 10(c,d)] and wormlike structure [Fig. 10(e,f)] with significantly greater diameters (widths) than heights (thicknesses) were observed, which also strongly suggested these aggregates collapsed on mica during the drying process. These observations could be attributed to the following two factors: first, the miktoarm star copolymers should probably spread out on the surface due to similar polarity of the hydrophilic PAA blocks and mica; on the other hand, it has been established that crystallization of PCL occurs by the formation of folded chain structures within a lamellar lattice, the formation of collapsed lamellar structures were probably driven by the crystallization of the PCL blocks during the drying process.[73] Melting temperature of PCL ($T_{m,PCL}$) was clearly detected in the DSC curves of these samples in solid state obtained by lyophilization (Supporting Information Fig. S3), which provides convincing evidence for this assumption.

CONCLUSIONS

Well-defined cyclodextrin-centered $A_{14}B_7$ multimiktoarm star copolymers [CDS(PCL-P*t*BA)] were successfully synthesized via the combination of CROP and ATRP from a β-CD derivative. ^{1}H NMR and SEC-MALLS analyses confirmed the designed structures. Selective hydrolysis of the P*t*BA block by TFA gave the amphiphilic $A_{14}B_7$ multimiktoarm star copolymers [CDS(PCL-PAA)]. These copolymers could self-assemble into various morphologies in aqueous solution, which can be controlled by both the macromolecular architecture and the composition of the copolymers. AFM measurements implied that the aggregates self-assembled from these miktoarm star copolymers had highly collapsed structures on mica surfaces probably owing to the driven force of the PCL crystallization process. What roles did the $A_{14}B_7$ multimiktoarm star architecture play in the self-assembly were still unclear, which is currently investigated in our laboratory.

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